

## Description

**PRODUCTION METHOD FOR OXIDATION-RESISTANT HIGH CHROMIUM  
FERRITIC HEAT RESISTANT STEEL**

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**Technical Field**

The invention of this application relates to a method for producing ferritic heat-resistant steel for use in boilers of thermal power plants, chemical industry apparatuses, and the like that are operated at high temperatures and under low oxygen partial pressure atmospheres.

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**Background Art**

In our country, about 60% of the total electric power demand is supplied by thermal electric power plants using fossil fuels; however, large amount of carbon dioxide is being emitted by the combustion of fossil fuels.

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On the other hand, higher power generation efficiency is strongly demanded on thermal power plants in view of the emission regulations on carbon dioxide for the prevention of global warming or from the viewpoint of effective use of resource energy. Heat resistant steel and heat resistant alloys have been used as materials resisting to high temperatures and high pressures at thermal power plants; in the case of using such heat resistant steel and heat resistant alloys under the atmosphere, dense oxide coating film forms on the surface to function as protective layers.

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However, in the presence of high temperature water vapor under low oxygen partial pressure atmospheric condition as such in thermal power plant boilers, the apparatuses used under such conditions suffer greater oxidation damage as compared

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with those used under atmospheric conditions, because the supply of oxygen is not sufficient to form protective coating films.

In general, Cr-containing heat resistant steel and heat-resistant alloys having a Cr content of 25 mass% or more show excellent oxidation-resistance because oxidation-resistant protective film is formed even under high temperature water vapor atmospheric condition.

Furthermore, in the case of chromium (Cr)-containing heat resistant steel and heat-resistant alloys having a Cr content of or about 20 mass%, it is possible to modify the surface of the base material by applying a mechanical treatment such as shot peening, or to form an oxidation-resistant protective coating film by a method such as crystal grain refining treatment and the like.

However, in the case of a high Cr ferritic heat-resistant steel containing 15 mass% or less of Cr, the Cr content is too low to supply the Cr oxide necessary for forming the oxidation-resistant protective coating film. Accordingly, as methods for ameliorating the oxidation resistance of a high Cr ferritic heat-resistant steel containing 15 mass% or less of Cr, attempts such as increasing chromium (Cr) or silicon (Si), or adding palladium (Pd) or platinum (Pt), etc., have been made (see, for example, literatures 1 ~ 4); however, they could not avoid the deterioration of the quality of material or the increase in cost due to the addition of elements such as palladium (Pd), platinum (Pt), etc. As described above, an effective method for improving the oxidation resistance of a high Cr ferritic heat-resistant steel containing 15 mass% or less, for instance, 9 to 12 mass%, is yet to be realized.

Literature 1; JP-A-2002-69531

Literature 2; JP-A-2001-192730

Literature 3; JP-A-11-61342

**Literature 4; JP-A-10-287960**

The invention of the present application has been made under such circumstances, and the objectives thereof are to overcome the problems of the conventional techniques and to provide a high Cr ferritic heat-resistant steel on which an oxidation-resistant protective coating film is formed even in the presence of high temperature water vapor under low oxygen partial pressure atmospheric condition.

**Disclosure of the Invention**

As a solution for the aforementioned problems, the invention of the application provides the invention as follows.

That is, the invention of the present application provides, firstly, a steel characterized in that it is a ferritic heat-resistant steel containing 15 mass% or less of Cr, in which at least the region up to 10  $\mu\text{m}$  defined by surface depth is made of a worked texture composed of extended ferritic grains or superfine texture composed of ferrites 3  $\mu\text{m}$  or less in grain diameter, and having a protective coating film on the surface. Secondly, it provides a steel characterized in that the shorter diameter of the extended ferritic grains is 5  $\mu\text{m}$  or less; and thirdly, it provides a steel characterized in that the shorter diameter of the extended ferritic grains is 3  $\mu\text{m}$  or less, or the grain diameter of the ferrites is 1  $\mu\text{m}$  or less.

The invention of the present application provides, fourthly, a production method for a steel of one of claims 1 to 3, in which working is applied in the temperature range of from 400 to 800°C to form a worked texture or superfine ferrite grain texture at least in the region up to 10  $\mu\text{m}$  defined by surface depth, and pre-oxidation treatment is applied to form a protective coating film; fifthly, it provides a production method in which the working degree on applying working is 0.7 or higher in true strain; and sixthly, a

production method in which the pre-oxidation treatment is carried out by holding the steel for 30 to 90 minutes in the temperature range of from 400 to 800°C under the atmosphere.

## 5    **Brief Description of the Drawings**

Fig. 1 is a cross sectional scanning electron microscope (SEM) photograph of an intensively worked part which have been subjected to compression working at a temperature of 500°C, followed by pre-oxidation treatment in the atmosphere at 640°C/1h, an then by water-vapor oxidation at 650°C/100h;

10    Fig. 2 is a cross sectional SEM photograph of a weakly worked part which have been subjected to compression working at a temperature of 500°C, followed by pre-oxidation treatment in the atmosphere at 640°C/1h, an then by water-vapor oxidation at 650°C/100h; and

Fig. 3 is side cross sectional SEM photograph of an intensively worked part which  
15    have been subjected to compression working at a temperature of 500°C, followed by water-vapor oxidation at 650°C/3h without applying pre-oxidation treatment.

## **Best Mode for Carrying Out the Invention**

The invention of the application has the above characteristics, and the mode of  
20    carrying out the invention is described below.

First of all, in ameliorating the oxidation resistance of a high Cr ferritic heat-resistant steel containing 15 mass% or less of Cr even in the presence of high temperature water vapor or under low oxygen partial pressure atmospheric condition, the invention of the application is most characterized by that the oxidation resistance is  
25    improved by applying a specific working and heat-treatment, and not by increasing the

composition of chromium (Cr) or silicon (Si), nor by adding elements such as palladium (Pd) or platinum (Pt) and the like. Accordingly, the high Cr ferritic heat-resistant steel obtained by the method for improving the oxidation resistance according to the invention of the application possesses an advantage in that the physical properties and the chemical  
5 properties of the initial composition remain without being impaired.

In general, in case the Cr content exceeds 15 mass%, as described above, the surface layer of the steel material can be modified by applying mechanical treatment such as shot peening and the like, or an oxidation-resistant protective coating film can be formed by applying relatively mild crystal grain refining treatment with large grains  
10 about 10 to 50  $\mu\text{m}$  in particle diameter, however, in high Cr ferritic heat-resistant steel containing 15 mass% or less Cr, such oxidation-resistant protective coating film cannot be formed even if such treatment should be employed. The reason for the above is because, in case the Cr content is 15 mass% or less, Cr necessary for forming the protective coating film containing  $\text{Cr}_2\text{O}_3$  as the principal component cannot be  
15 sufficiently and uniformly diffused even if the crystal grain refining treatment for obtaining crystals about 10 to 15  $\mu\text{m}$  in grain diameters should be applied. Accordingly, oxidation-resistant protective coating film cannot be formed in the presence of water vapor under high temperatures.

Thus, the keys of the invention of the present application are to accumulate strain  
20 energy at high levels by applying warm intensive working to the high Cr ferritic heat-resistant steel, or to form fine texture consisting of crystal grains 2  $\mu\text{m}$  or less in grain diameter. In the invention of the application, the reason for accumulating strain energy at high levels or for forming fine texture consisting of crystals grains 3  $\mu\text{m}$  or less in grain diameter is because, the steel material having the strain energy accumulated in  
25 high levels easily undergoes recrystallization to form superfine grain texture. Thus,

with the formation of the superfine grain texture above, the grain boundary area increases to contribute for the diffusion acceleration of chromium (Cr). Then, by the uniform diffusion of chromium (Cr), chromium oxide ( $\text{Cr}_2\text{O}_3$ ) is formed to function as an oxidation-resistant protective coating film. As described above, the strain energy is highly accumulated in the invention of the application. Further, the formation of superfine grain texture consisting of ferrite grains  $3\text{ }\mu\text{m}$  or less in grain diameter may be considered as a mode of accumulating the strain energy at a high level.

By the thermomechanical treatment such as the rolling or the forging generally employed in the art, it is not possible to highly accumulate the strain energy or to form a fine texture consisting of ferritic crystal grains  $3\text{ }\mu\text{m}$  or less in grain diameter according to the invention of the present application. In order to highly accumulate the strain energy or to form the fine crystal grain texture consisting of crystal grains  $3\text{ }\mu\text{m}$  or less in grain diameter, it is preferred to perform warm working treatment at a strain rate of  $0.1\text{sec}^{-1}$  or higher and at a working ratio (cross section area reduction ratio) of 70 % or higher. In case the working ratio is lower than 70 %, the accumulation of the desired strain energy remains insufficient, and the generation of protective coating film and the use thereof cannot be fully expected ever after the pre-oxidation treatment.

Considering the warm intense working, it is preferably carried out in the temperature range of 400 to  $800^\circ\text{C}$ . Further, by forming the strain under the conditions above, it is possible to generate the elongated ferritic grains or fine grains.

As the morphology of the elongated ferritic grains, it is preferred that it has a shorter diameter of  $5\text{ }\mu\text{m}$  or less, and most preferably, it has a shorter diameter of  $3\text{ }\mu\text{m}$  or less; otherwise, the ferritic grains has a grain diameter of  $3\text{ }\mu\text{m}$  or less, and most preferably, they are fine grains  $1\text{ }\mu\text{m}$  or less in grain diameter.

As described above, the invention of the present application comprises

accumulating strain energy at high levels by applying warm intensive working to the high Cr ferritic heat-resistant steel, or forming fine texture consisting of crystal grains 3  $\mu\text{m}$  or less in grain diameter; however, the protective coating film does not always form at high temperatures in the presence of water vapor by simply accumulating the strain energy by warm intensive working or by forming fine crystal texture. It is necessary to form sequentially thereafter the protective coating film by applying pre-oxidation treatment. The pre-oxidation treatment is preferably carried out under the atmosphere or under an inert gas (rare gas or gaseous nitrogen) atmosphere containing gaseous oxygen, but more practical is to perform the treatment in the atmosphere. Further, the pre-oxidation treatment is preferably performed by heat treatment in the atmosphere at 400 ~ 800°C for about 30 to 90 minutes.

By combining the heat treatments above, chromium (Cr) is oxidized for the first time, and forms  $\text{Cr}_2\text{O}_3$  which functions as an oxidation-resistant protective coating film.

Furthermore, concerning the relation between the heating temperature of the pre-oxidation treatment and the average crystal grain size, it is confirmed that, when heated under the atmosphere, the grain diameter is 0.8  $\mu\text{m}$  or less for the sample held at 660°C or lower, and is 1 ~ 2  $\mu\text{m}$  for the sample held at 680 ~ 700°C.

As described above, the invention of the application enables forming an oxidation-resistant protective coating film on the high Cr ferritic heat-resistant steel having a Cr content of 15 mass% or less, on which an oxidation-resistant protective coating film had never been formed, and this widely increases the usage of high Cr ferritic heat-resistant steel. Furthermore, the invention of the application is advantageous in that it utilizes heat treatment, because it does not make any changes on the composition of the high Cr ferric heat-resistant steel. Moreover, since the protective coating film is thin and is tightly adhered, it hardly peels off; it thereby exhibits effect on

greatly reducing the risk of causing clogging of the piping due to the peeled off scales, or of wearing the turbine blades.

It should be noted that the high Cr ferritic heat-resistant steel of the invention of the application includes those of various compositions containing 15 mass% or less of Cr.

5 For instance, there are included those containing 7 mass% to 15 mass% of Cr.

Steel, such as the high Cr ferrite heat-resistant steel specified in ASME SA335 P91 or ASME SA 213 T91, are included. These are specified in the invention of the application by the general term “high ferritic (system)” steel.

## 10 Examples

### <Example>

Mod. 9Cr-1Mo steel was subjected to 70% compression working at 500°C, and was cut and polished in such a manner that the fine texture region and the worked texture region should be exposed on the surface. Then, after applying pre-oxidation treatment at 650°C for 1 h in the atmosphere, the test specimen was oxidized in water vapor at 650°C/100 h. Fig. 1 shows the cross section SEM photograph of the intensively worked part. The formation of the Cr-rich ( $\text{Cr}_2\text{O}_3$ ) protective coating film (0.1  $\mu\text{m}$  or less in thickness) on the surface was observed. Furthermore, the crystal grain diameter of the ferritic grains in the fine texture region under the protective coating film was found to be 1.0  $\mu\text{m}$  or smaller. Further, the shorter diameter of the elongated ferrite in the worked texture region under the protective coating film was found to be 3  $\mu\text{m}$ .

### <Comparative Example 1>

Mod. 9Cr-1Mo steel was subjected to pre-oxidation treatment at 680°C for 1 h in the atmosphere, and was then subjected to water-vapor oxidation at 650°C/100 h. Fig. 2 shows the cross section SEM photograph of the resulting product, but the growth of an



Fe-rich double layer scale (about 60  $\mu\text{m}$  in thickness) due to accelerated oxidation was observed. The average grain diameter of the ferritic grains was 7  $\mu\text{m}$ .

By comparing the above result with that of the Example, it was confirmed that the high accumulation of strain energy or the formation of fine crystal texture is necessary to form a protective coating film having resistance against water-vapor oxidation.

#### **<Comparative Example 2>**

Mod. 9Cr-1Mo steel was subjected to 70% compression working at 500°C in a manner similar to that of Example 1, and was subjected to water-vapor oxidation at 650°C/3 h thereafter without applying pre-oxidation treatment for observation. Fig. 3 shows the cross section SEM photograph of the intensively worked part. The formation of double layer scale (about 10  $\mu\text{m}$  in thickness) was observed.

#### **Industrial Applicability**

As described in detail above, the invention of the application enables forming a thin and highly adhesive oxidation-resistant protective coating film, which had been believed impossible, on the high Cr ferritic steel having a Cr content of 15 % or less.